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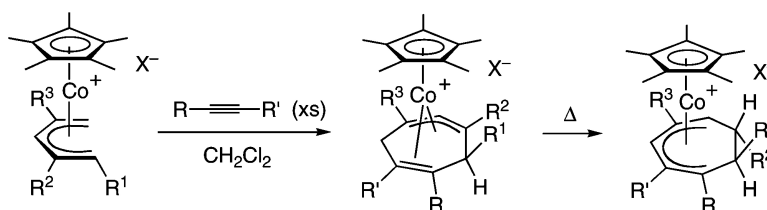
Cobalt-Mediated ￼-Pentadienyl/Alkyne [5 + 2] Cycloaddition. Synthesis and Characterization of Unbridged ￼,￼-Coordinated Cycloheptadienyl Complexes

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Cobalt-Mediated η^5-Pentadienyl/Alkyne [5 + 2] Cycloaddition. Synthesis and Characterization of Unbridged η^2,η^3-Coordinated Cycloheptadienyl Complexes

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Novel transition metal-mediated reactivity patterns provide the conceptual basis for the development of new synthetic reactions. Particularly for larger ring systems, metal-mediated cycloaddition pathways can provide convergent access to a range of substituted and functionalized carbocyclic systems that would be otherwise laborious to prepare.[1] The [5 + 2] cycloaddition of an alkyne and η^5-pentadienyl complex remains an unsolved problem, despite considerable effort.[2] Without exception, the reaction suffers from limited scope, low yields, and/or poor product control, often preferentially proceeding to higher order cycloadducts incorporating additional alkyne.[3]

To evaluate the hypothesis that a cobalt-mediated [5 + 2] alkyne/η^5-pentadienyl cycloaddition (III→IV, eq 1) might be embedded in the mechanism of our recently reported η^3-cyclopentenyl/alkyne ring expansion reaction (I→IV),[4] we initiated an investigation into the preparation and reactivity of acyclic (open) η^5-pentadienyl cobalt complexes. Although the transformation of agostic η^3-cyclopentenyl complexes to ring-opened η^5-pentadienyl products (e.g., II→III) has been demonstrated in the solid state at elevated temperature,[5] the reactivity of cobalt η^5-pentadienyl complexes toward alkynes is unknown.
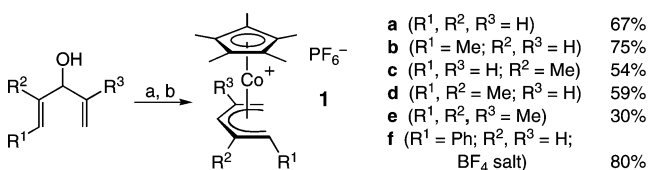
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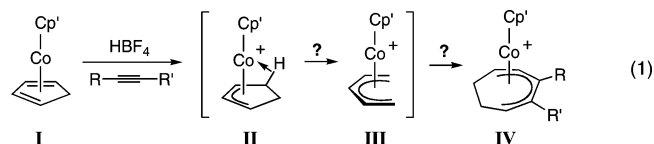
Here we report the discovery of a general [5 + 2] cycloaddition reaction, providing seven-membered ring complexes in high yield under notably mild conditions. For some substituent arrays, the reaction proceeds with high selectivity to give the cycloheptadienyl ring as the η^2,η^3-coordinated isomer, *an unprecedented coordination mode for unbridged cycloheptadienyl systems*.[6–9] Subsequent isomerization to the fully conjugated η^5-cycloheptadienyl product occurs under thermodynamic control.

Acyclic η^5-pentadienyl complexes of cobalt are known but are rare.[5,10,11] An efficient and reasonably general entry into the synthesis of the requisite cationic η^5-pentadienyl complexes **1** has been developed by adapting a ligand exchange/protonolysis strategy previously reported for converting *conjugated* dienols to pentadienyl complexes of rhodium and iridium.[12]

Thus, readily available 1,4-alkadien-3-ol substrates typically associated with the Nazarov cyclization[13] react with HBF$_4$•OEt$_2$ and (C$_5$Me$_5$)Co(C$_2$H$_4$)$_2$[14] to afford η^5-pentadienyl complexes **1** in reasonable isolated yields (Scheme 1).[15] The reaction gradually diminishes in utility with increasing substitution of the substrate, presumably due to competing off-metal cyclization/oligomerization pathways. The air-stable complexes are readily isolated and purified by chromatography on the bench.[16] In addition to new complexes **1a–f**, the corresponding η^5-1-ethylpentadienyl complex **1g** was prepared as the BF$_4$ salt according to the previously published procedure.[5b]

Although coordinatively saturated, 1-substituted pentadienyl complexes **1b**, **1f**, and **1g** incorporate alkyne thermally even at room

Scheme 1 *a*

a (R^1, R^2, R^3 = H)	67%
b (R^1 = Me; R^2, R^3 = H)	75%
c (R^1, R^3 = H; R^2 = Me)	54%
d (R^1, R^2 = Me; R^3 = H)	59%
e (R^1, R^2, R^3 = Me)	30%
f (R^1 = Ph; R^2, R^3 = H; BF$_4$ salt)	80%

a Conditions: (a) Cp*Co(CH$_2$CH$_2$)$_2$, HBF$_4$•OEt$_2$, acetone, −78 °C; (b) KPF$_6$, H$_2$O (not performed for **1f**).

temperature (eq 2, Table 1). Reactions with excess acetylene proceed slowly (entries 1, 6, and 9), providing *nonconjugated η^2,η^3*-cycloheptadienyl cycloadducts **2** with excellent selectivity. The structures of the products were unambiguously determined by spectroscopic analysis and confirmed for complex **2a** by X-ray crystallography.[15]

All three η^2,η^3-cycloadducts isomerize quantitatively to the fully conjugated η^5-cycloheptadienyl complexes **3b**, **3f**, and **3i** upon heating; the more reactive phenyl derivative **2f** converts slowly even at room temperature.[15] Cycloaddition reactions incorporating 2-butyne proceed slowly but quantitatively (entries 2 and 7). In these cases, however, the rate of cycloadduct isomerization is competitive with the rate of the initial cycloaddition, rendering it impossible to isolate the η^2,η^3-cycloheptadienyl intermediates selectively.[17] This situation is maintained for the reactions of the terminal alkynes, 1-pentyne and ethoxyacetylene (entries 3 and 4), which afford η^5-cycloadducts in excellent yields. Neither reaction, however, shows appreciable steric or electronic control over the regioselectivity of alkyne insertion. Cycloaddition of the more sterically demanding trimethylsilylethyne with 1-phenylpentadienyl complex **1f** proceeds to a single η^5-cycloadduct **3h** (entry 8), albeit in greatly diminished yield.[18] Confirmation of the structure of **3h** was obtained by X-ray crystallography.[15]

To our considerable consternation, terminally unsubstituted pentadienyl complexes exhibit significantly attenuated reactivity toward alkynes. Neither the unsubstituted pentadienyl nor 2-methylpentadienyl complex (**1a**, **1c**) reacts with ethyne or 2-butyne at or below 40 °C; both convert slowly at 60 °C but give only intractable product mixtures. The more highly substituted 1,2,4-trimethylpentadienyl complex **1e** is similarly inert, consistent with the greater stability noted for ancillary pentadienyl ligands alkylated in the 2- and 4-positions.[11,19] Significantly, however, the 1,2-dimethylpentadienyl complex **1d** is more promising, reacting with ethyne at 60 °C (16 h) to yield a mixture of η^2,η^3- and η^5-cycloadducts **2e** and **3e**, strongly—and surprisingly—biased toward the kinetic η^2,η^3-isomer (entry 5).

Mechanistically, these results are consistent with a *dissociative process* initiated by an $\eta^5→\eta^3$ pentadienyl isomerization (Scheme 2), which is unexpectedly facile for pentadienyl ligands bearing terminal substituents. Subsequent alkyne coordination, insertion, and transannular cyclization are fully consistent with conceptually related [3 + 2 + 2] allyl/alkyne cycloaddition reactions.[6e–g,7] Most unusual, however, is the determination that the kinetic barrier to cycloheptadienyl valence isomerization from η^2,η^3- to η^5-coordina-

Table 1. Cyclohepatadienyl Synthesis by [5 + 2] Cycloaddition[a]

entry	substrate	alkyne	2/yield (%)[b]	3/yield (%)[c]
1	**1b** (R^1 = Me; R^2, R^3 = H)	R, R' = H	**2a**/98	**3a**/99
2	**1b**	R, R' = Me	−	**3b**/99
3	**1b**	R = H R' = OEt	−	**3c:3c'** (2:1)/82 **3c**: R = H, R' = OEt **3c'**: R = OEt, R' = H
4	**1b**	R = H R' = ^{n}Pr	−	**3d:3d'** (2:1)/91 **3d**: R = H, R' = ^{n}Pr **3d'**: R = ^{n}Pr, R' = H
5[c]	**1d** (R^1, R^2 = Me; R^3 = H)	R, R' = H	**2e** + **3e** (3.8:1)/68[d]	
6	**1f** (R^1 = Ph; R^2, R^3 = H)	R, R' = H	**2f**/89	**3f**/99
7	**1f**	R, R' = Me	−	**3g**/96
8	**1f**	R = H R' = TMS	−	**3h**/26[e] R = H, R' = TMS
9	**1g** (R^1 = Et; R^2, R^3 = H)	R, R' = H	**2i**/91	**3i**/99

[a] Detailed conditions reported in the Supporting Information; yields of isolated products after SiO$_2$ chromatography (3−4% MeOH in CH$_2$Cl$_2$). [b] Ethyne (saturated solution in CH$_2$Cl$_2$), rt, 12−20 h. Minor amounts of the fully conjugated product **3** are detectable by NMR spectroscopy. [c] As above but 40−60 °C, 24−72 h (rt, 72 h for **3g**). [d] An additional minor byproduct, tentatively identified as a [3 + 2 + 2] cycloadduct, is detected in the NMR spectrum of this product.[15] [e] Yield determined by ^{1}H NMR integration using 1,3,5-trimethoxybenzene as an internal standard.

Scheme 2
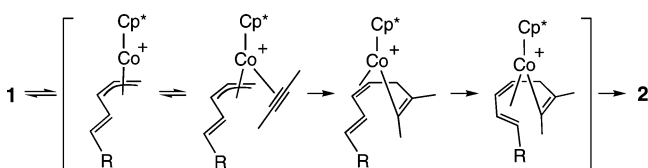
tion is rate-limiting in this system, allowing isolation and, we presume, exploitation of the novel η^2,η^3-coordination mode.[20]

Cobalt-mediated [5 + 2] cycloaddition represents a general new reaction for the convergent synthesis of seven-membered rings. In combination with post-cycloaddition alkylation/demetalation strategies, currently in development, the process can be construed as a novel "interrupted Nazarov" cyclization,[21] in which the cationic intermediate is intercepted prior to the electrocyclization.

Supporting Information Available: Experimental procedures and complete characterization data for all new compounds; details of the X-ray crystallography for complexes **2a** and **3h**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(15) Complete experimental details are provided as Supporting Information.

(16) Complexes **1b**−**f** have also been characterized by X-ray crystallography; details will be provided in a subsequent report.

(17) Spectroscopic analysis of the reaction of **1b** with 2-butyne at intermediate times (ca. 40% conversion) reveals the presence of both η^2,η^3- and η^5-cycloadducts **2b** and **3b**, with **2b** in low concentration. Complete conversion to **3b** is obtained upon prolonged reaction time, establishing that *the η^2,η^3-isomer is an intermediate in the formation of the η^5-cycloadduct*.

(18) A single cycloheptadienyl product was detected spectroscopically in the complex reaction mixture. No tractable product is isolated from reactions of 1-methylpentadienyl complex **1b** with *tert*-butyl-, trimethylsilyl-, or phenylacetylene, which return complex, partly paramagnetic mixtures.

(19) Preliminary investigation suggests that the reactivity in the parent (cyclopentadienyl)cobalt series is enhanced, allowing the [5 + 2] cycloaddition reaction to proceed even with the unsubstituted pentadienyl complex.

(20) Alkylation/oxidative decomplexation protocols for demetallation of the organic remain under investigation; for related reactions, see ref 6f.

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